Degradation of Toxic Chemicals by Zero-Valent Metal Nanoparticles - A Literature Review

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ABSTRACT

The ultimate aim of researchers in the area of decontamination is to develop the perfect decontaminant - a substance that will degrade all contaminants but will leave surfaces and environments unharmed. Published research into zero-valent metal particles (ZVMs), in particular iron, shows that these particles, particularly those whose size is on the nanoscale, have the potential to be used as a decontaminant. This report examines the literature on nanoscale ZVMs, their potential use as decontaminants and ways to enhance their activity. Most of the research to date has looked at the reductive potential of ZVMs but it has been reported that zero-valent iron (ZVI) can actually catalyse oxidative degradation in a Fenton-type reaction. Thus this report also explores Fenton-type degradation of chemical warfare agents. The report also examines methods of incorporating nanoscale ZVM particles onto solid supports which may be useful for increasing the lifetime, activity and usability of the particles. Finally, possible challenges to developing ZVMs as a decontaminant are discussed.

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Degradation of Toxic Chemicals by Zero-Valent Metal Nanoparticles - A Literature Review

Executive Summary

Decontamination, commonly described as the removal or destruction of toxic substances, is an important aspect of operations in a chemically or biologically contaminated environment. For this reason the military is always looking for the perfect decontaminant. The ultimate decontaminant is a product that will destroy all toxic contaminants without any adverse effects on surfaces or the environment. For this reason it is vital to military operations that researchers aim to develop such a decontaminant.

Prior research into zero-valent metal particles (ZVMs) has shown that there is some potential to their use as a decontaminant. This report examines those research efforts from the perspective of the use of ZVMs as a potential decontaminant for toxic chemical compounds of military interest. It is observed that reducing the size of these particles to the nanoscale vastly increases their reactivity. Other ways to increase activity, such as using bimetallic particles (where two different metals are fused together in each particle), using additives (surfactants) that increase the solubility of certain contaminants in water or using ultrasound, show promise in creating a very good decontaminant. Different ways of incorporating the particles, for example onto polymeric supports, potentially broadens their applications without significantly affecting their reactivity.

While there are challenges, such as particle stability (limited lifetime) and possible toxic by-products, to the development of ZVMs as a decontaminant there are promising studies that show that these issues may be overcome or at least significantly reduced. This technology is worthwhile investigating and developing further as it shows great promise for the destruction of toxic substances of military interest.

Contents

1. Introduction

Decontamination is an important aspect of operations in a chemically or biologically contaminated environment. For this reason the military are always looking for the perfect decontaminant. Development of such a 'perfect decontaminant' is the ultimate aim of decontamination practitioners, that is, to develop a decontaminant that can be used for all applications and situations. To achieve this aim there are certain criteria that must be kept in mind when developing a decontaminant. It is necessary for a decontaminant to achieve complete destruction of the contaminant as fast as possible. Logistical considerations further emphasise the need for a highly reactive decontaminant. A conflicting requirement is for the decontaminant to be non-destructive to surfaces/substrates such as paints and rubbers. This leads to the difficult situation of developing a decontaminant that is selective to all contaminants but nothing else. It also should have no detrimental affect on sensitive equipment, particularly monitors and detectors nor should it interfere in the response of these instruments. Ease of application is also a desirable feature for logistic and training reasons.

The use of zero-valent metal particles for decontamination of common soil and water contaminants has been the subject of many studies. These zero-valent metal particles show some promise in fulfilling the above requirements.

Most studies of the degradation of organic chemicals by zero-valent metal particles have focused on the reductive mechanisms. However, zero-valent metal particles can also be used to initiate oxidative reactions. Oxidative reactions are of primary interest to us as they have the potential to degrade organophosphorous nerve agents as well as vesicants such as mustard. Only the vesicants, which contain carbon-chlorine bonds, are degraded by reduction. Figure 1.1 shows the structures of a) mustard and b) nerve agent (general structure). To decontaminate mustard there are two approaches, dechlorination or oxidation of the sulfur, the later of which is preferable due to the reversibility of the former. To decontaminate the nerve agents oxidation is required to replace X_2, X_3 and, in some cases, X_1 to produce the appropriate phosphonic acid. Hydrolysis is also possible for both nerve and mustard agent degradation however this review focuses or redox type reactions.

Where:
X_1 is R or RO
X_2 is most commonly F; CN or $S(CH_2)_nNR2$
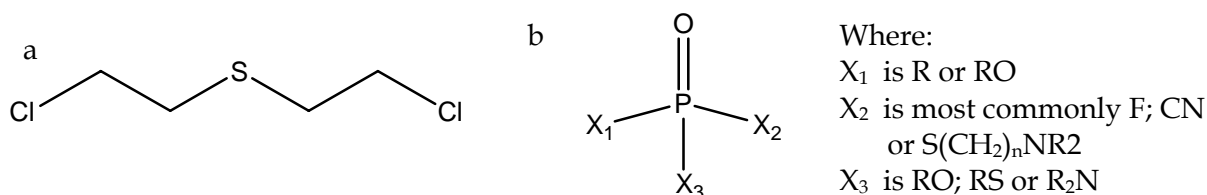X_3 is RO; RS or R_2N

Figure 1.1: a) Structure of Mustard and b) General Structure of Nerve Agents

Zero-valent iron (ZVI) has been the main focus of zero-valent metal particle studies but zinc, tin and magnesium have also been studied as well as some bimetallic particles. Iron is commonly studied due to its low cost and non-toxicity. So far, iron is the only zero valent particle to be studied for its oxidative degradation properties.

The primary application of ZVI-catalysed degradation that has been looked at is its use in permeable reactive barriers to decontaminate water. These are designed to go in-situ into a contaminated water flow, primarily groundwater. Such barriers incorporate mainly granular iron particles. However, the increase in surface area and energy gained by using nanoscale particles increases the decontamination potential of the particles. Another important consideration in the effectiveness of ZVI is the way in which the catalyst particles are incorporated into the system. A variety of solid supports may be used or particles can be incorporated into polymer shells or matrices.

2. Reductive Mechanisms

The majority of work surrounding the reductive capacity of zero-valent metals has focused on halogenated hydrocarbon (specifically chlorinated) contamination of water, although nitrate [1], Cr(VI) and Pb(II) [2, 3], s-triazines [4], RDX [5] and perchlorate [6] have also been examined.

For a general review of the use of reductive mechanisms in permeable reactive iron barriers see Tratnyek et al.[7]

2.1 Mechanisms of Reductive Dechlorination

Degradation of chlorinated hydrocarbons can occur by four reductive mechanisms, three of which can be classified as dehalogenation reactions. These are hydrogenolysis (reaction 2.1), elimination, can be β-elimination (reaction 2.2a) or α-elimination (reaction 2.2b, proceeds via a carbene intermediate), dehydrohalogenation (reaction 2.3) and hydrogenation (reaction 2.4). [7-10]

$$Cl_2C=CCl_2 + H^+ + 2e^- \rightarrow Cl_2C=CClH + Cl^- \qquad \ldots(2.1)$$
$$Cl_2C=CCl_2 + 2e^- \rightarrow ClC{\equiv}CCl + 2Cl^- \qquad \ldots(2.2a)$$
$$CCl_3H \rightarrow {:}CCl_2 + HCl \rightarrow \text{ variety of products} \qquad \ldots(2.2b)$$
$$RCl_2C-CClHR' \rightarrow RClC=CClR' + H^+ + Cl^- \qquad \ldots(2.3)$$
$$RClC=CClR + H_2 \rightarrow RHClC-CClHR \qquad \ldots(2.4)$$
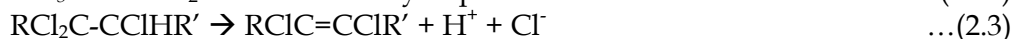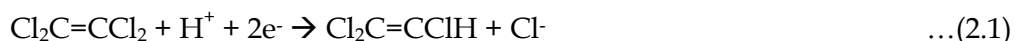
Reactions 2.1 and 2.2a are the dominant reaction pathways, with the major pathway determined by reaction conditions.

More information on the mechanisms and pathways of reductive zero-valent metal processes are readily available.[see for example 7, 10-14]

2.2 Kinetics of Reductive Dechlorination

It is apparent that proton availability may influence the rate of reaction 2.1. It has been observed that the rate of hydrogenolysis of carbon tetrachloride by ZVI increases linearly with decreasing pH.[9] However the relationship between bulk pH and availability of protons at the metal surface is unknown. Kinetic studies by Matheson and Tratnyek showed that the order of reaction with respect to protons is approximately 0.15 indicating that protons are not involved in the rate-determining step but are an indirect effect (such as enhancing iron corrosion in aqueous environments).[9] Observations by Chen et al [15] suggest that there is a trade-off between the increased degradation rate constant of trichloroethylene (TCE) at lower pH's and the consumption of ZVI by corrosion thus effectively decreasing the surface area. They found that there was a maximum in the degradation rate at a pH of 4.9.

Hydrogenolysis via ZVI particles appears to be diffusion controlled, at least for carbon tetrachloride, as reaction rates increase with mixing vigour, and temperature changes have no significant effect on the reaction rate (i.e. activation energy of reaction is small).[9] Dechlorination follows pseudo first-order kinetics as shown in equation 2.5 where C is the concentration of the chlorinated contaminant.

$$\frac{dC}{dt} = -k_{obs} C \qquad \qquad \qquad \ldots (2.5)$$

The most important factor that influences k_{obs} is the surface area of the zero-valent metal,[9] although other work by Chen et al [15] suggests that cleanliness of surface is more important than surface area. The influence of surface area will be discussed in Section 4.

Further information on the kinetics of the reductive processes of zero-valent metals is readily available.[see for example 1, 6, 7, 9, 10, 13, 16-19]

2.3 Zinc Versus Iron

While iron is the most extensively examined metal for reductive processes like dechlorination, other metals including zinc, tin and magnesium have also been looked at.[20] Apart from iron, zinc is the most extensively studied zero-valent metal.[10-13, 20-22]

Zinc (and tin) can degrade halogenated hydrocarbons both faster[20, 23] and more completely than iron.[21] According to Cheng and Wu the greater reduction potential of zinc and its high hydrogen overvoltage make it a better choice for reductive degradation of chlorinated hydrocarbons.[22] They found that the half-life with zinc particles was one-tenth that with iron particles.

However zinc reacts with oxygen to form passivating zinc oxides, which then inhibit the zinc's reactivity as the reactants cannot penetrate the passivating layer.[24] Iron oxides are non-passivating which allows the reactants to penetrate the oxide layer and react with the active iron surface.

There is evidence that the mechanism by which zinc reduces halogenated hydrocarbons is different to that of iron.[13] For halogenated ethylene compounds the less halogenated the ethylene the faster it reacts with iron. With zinc it is the other way around.

2.4 Zero-Valent Silicon

Zero-valent silicon (ZVS) is a strong reducing agent with $E° = -0.857V$. This means that it can act as an electron donor to halocarbons in a hydrogenolysis reaction (of the type reaction 2.1) according to:

$$Si^0 + 2RX + 3H_2O \rightarrow H_2SiO_3 + 2RH + 2H^+ + 2X^- \qquad \ldots(2.6)$$
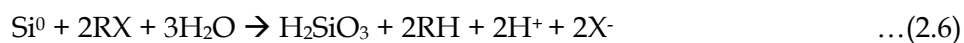
Sequential first-order hydrogenolysis is the main reaction pathway identified in the Si^0-H_2O system. A lag time (defined by Doong et al as the time required to detect 10% reduction of chlorinated contaminant) was observed in this system and was found to decrease with increasing pH. This is consistent with the thought that the lag time was due to the hydrogen-terminated surface of the silicon and the formation of SiO_2 on the surface. The hydroxide ions remove the surface bound hydrogen atoms and SiO_2 can be solubilized in basic conditions to form $HSiO_3^-$. In addition to decreasing the lag time an increase in pH caused a linear increase in the normalised surface degradation rate constant for carbon tetrachloride and thus the degradation rate was shown to be first order with respect to pH.[8] It is also apparent from reaction 2.6 that a high pH will aid the reaction in going to completion.

Combining ZVS with ZVI appears to overcome the problems associated with using both in isolation. There is no lag time in the combined system as the iron initially dominates the reductive dechlorination reactions. At high pHs a ZVI system becomes ineffective due to the formation of iron oxides and as the ZVI reacts it forms hydroxide ions, which increase the pH; for this reason it is normally buffered. However in the ZVI/ZVS system the ZVS itself acts as a buffer by consuming the hydroxide ions that are produced by the iron in its own oxidation reaction. This means that the pH does not continue to rise and the iron does not become ineffective and the rate of dechlorination is accelerated compared to an

unbuffered ZVI system. While the silicon controls the pH, the iron controls the end products indicating that it dominates in the reaction.[8]

The major advantage of this ZVI/ZVS system is seen in the fact that ZVS is a solid, an effective buffer to the ZVI and produces environmentally friendly ions when oxidised as happens in the ZVI/ZVS system.[8] In a permeable reactive barrier placed in a groundwater system there is no practical way to buffer the ZVI with conventional buffers thus combining with ZVS may aid the rate of degradation.

2.5 Bimetallic Particles

Bimetallic particles are those particles on which a thin layer of catalytic metal (eg Pd, Pt, which are not active in themselves) is doped onto the surface of the active (reducing) metal, Fe or Zn. As well as catalysing the dechlorination reaction, such bi-metallic particles have been found to reduce the amount of toxic chlorinated by-products, indicating that the dechlorination reactions continue further towards completion.[24, 25] In one study no chlorinated products were detected above the 5µg/l detection limit.[26] Palladium has been found to be the most active catalyst,[24] but other metals, such as platinum and nickel, have also been found to be effective.[22, 24, 25] Physically mixing the two metals does not increase the rate of reaction, the palladium must be doped onto the surface.[24] Doping palladium on the surface sets up a galvanic couple, which increases the rate of corrosion of the iron thus increasing the rate of dechlorination.[26] Palladium and nickel have also been found to significantly enhance the dechlorination of polychloroethylene (PCE) in a zero-valent silicon/water system.[8]

Another advantage of these bimetallic particles is that they can add stability; ZVI particles underwent surface oxidation within a few hours (black to reddish-brown) whereas palladium modified iron particles did not undergo an observable colour change in air – suggesting stability.[24] Correspondingly the ZVI particles lose reactivity within a few days while Fe/Pd particles remain active for at least two weeks.[26] This appears to be despite the fact that the galvanic couple increases the iron corrosion rate during dechlorination reactions.[26] Doping the zinc surface with palladium can also prevent passivation occurring.[24]

Cheng and Wu found that bimetallic particles could aid in the dechlorination of TCE, where the reaction half-lives when using Fe, Fe/Ni and Fe/Pd particles were 239hrs, 3.9-5hrs and 1.3hrs respectively.[22] Similarly while Zn alone was found to produce a reaction half-life of 26.8hrs, this was decreased to 0.86hrs and 0.46hrs by the use of Zn/Ni and Zn/Pd respectively. Schrick et al also found that nanoscale Fe/Ni was not only more effective than nanoscale iron in degrading TCE, but also in preventing build-up of dichloroethylene (DCE) and vinyl chloride.[25]

Muftikian et al used X-ray photoelectron spectroscopy (XPS) to study the surface of Pd/Fe samples (these were not nanoparticles).[27] They found that a 'multilayer hydroxylated oxide film', with an outer layer of FeO(OH), covered the iron surface.

A reduction in the rate of dechlorination of TCE over time was observed with the palladized iron particles in studies by Muftikian et al.[27] They attributed this to an increase in the hydroxylated oxide film thickness making Pd atoms less accessible. Rinsing the particles with dilute acid restored the original activity of the particles.

It has been thought that nanoparticles may have a limited lifetime in a subsurface environment, however Lien and Zhang have observed reactivity of bimetallic nanoparticles after 6 months in soil-water slurries.[26]

Doping of ZVI with other metals does not always increase the rate of degradation. Inhibitive effects have been observed on pentachlorophenol degradation when ZVI was modified with Pd, Pt, Ni and Cu.[28].

2.6 Surfactant Effects

Halocarbon species can be adsorbed more readily onto a hydrophobic surface, or a surface where the immediate hydrophobic content is high, as this aids the partitioning of the halocarbon onto the surface from the bulk aqueous phase. For this reason a surfactant with a long hydrophilic chain may be useful in increasing the rate of the dehalogenation reaction that occurs on the ZVI surface. It was found in one study [reference 11 in 29] that the cationic surfactant hexadecyltrimethylammonium (HDTMA) increased PCE rate of degradation while the anionic surfactant, Sodium Dodecylsulfate (SDS), did not. Cationic surfactants are ideal for use in surface modification due to the fact that they adsorb strongly onto most solid surfaces.[29]

One of the problems associated with use of ZVI particles is that it requires a long contact time between the chlorocarbon and iron surface. By using surfactants that attract the organic species to the surface the contact time can be increased thus allowing a more complete reaction. This is particularly important when using ZVI in a permeable barrier where the contaminated water usually flows through. Increased sorption of PCE and TCE occurred as the surfactant concentration approached the critical micelle concentration (cmc) and then declined beyond that.[30] This is explained by the fact that as the amount of surfactant desorbed from the ZVI surface reaches the critical micelle concentration (cmc) micelles will form and the halocarbon will start to partition into the hydrophobic micelle core preventing access to the ZVI surface.[29] The rate of diffusion out of a micelle, and therefore the rate at which halocarbon will be released from the micelle, is inversely related to the hydrophobic chain length.[30] It was found however, that increased sorption did not lead to an increase in the reaction rate in the case of SDS. In the case of Triton X-100 (a non-ionic surfactant) increased sorption only increased the reaction rate of PCE at

concentrations close to its cmc and caused a build-up of TCE. Thus increased sorption alone is not sufficient to increase the rate of reaction.[30]

In the studies reported by Alessia and Li on the effects of cationic surfactants it was found that HDTMA had the highest maximum surfactant loading/sorption onto the ZVI particles and HDTMA-modified ZVI had higher degradation rate constants for PCE (12-19 times that of unmodified ZVI) than the other surfactants tested; i.e. octatrimethylammonium and dodecyl-trimethylammonium.[29] This corresponds to an increase in loading maxima and rate of degradation with an increase in the hydrophobic chain length. In most cases there was no significant adsorption of the bromide counter-ion (except possibly at higher loadings), which indicates that the sorbed surfactant molecules are mostly forming a 'patchy monolayer'. For all surfactants a higher loading did not result in an increase in dechlorination rate; in fact it was the reverse. This was attributed to higher surfactant loadings possibly forming a bilayer, which is now more hydrophilic, effectively blocking reduction sites from the chlorinated contaminant.[29]

It appears, at least in the case of PCE, that the presence of HDTMA encourages the degradation to proceed via hydrogenolysis as opposed to reductive elimination. The percentage of PCE accounted for by hydrogenolysis went from 10 to 35% as shown by TCE concentration. It is possible that the alkylammonium is acting as a Lewis acid in the crucial π-bond forming stage. Possibly addition of cationic surfactants in this manner may encourage the electron transfer process between chlorinated compound and ZVI surface.[29]

Changes in ionic strength were found not to significantly affect the degradation rate constant of PCE by HDTMA-modified ZVI[29] but an increase in ionic strength has previously been observed[reference 13 in 29] to increase the degradation rate of carbon tetrachloride by ZVI. pH was not a significant influence while it was low, but was found to essentially stop the reaction at pH 11 for PCE, whereas for TCE, carbon tetrachloride and vinyl chloride a significant reduction of reaction rate was observed at high pHs. This is consistent with iron oxide formation at high pHs.[29]

Addition of alcohol to a water/ZVI system caused the reaction rate to decrease to varying degrees. Surface sorption of PCE and TCE was also decreased by the addition of alcohols. Ethanol concentrations up to approximately 30% did not significantly decrease the rate and may be used to aid solubility of contaminants.[30] While addition of a surfactant above its cmc may also aid the solubility of a contaminant the rate of degradation is decreased as explained previously. Many other means of increasing solubility have a similar effect of sequestering the contaminant and thus separating it from the iron surface, see for example the use of hydroxypropyl-β-cyclodextrin by Bizzigotti et al.[31]

2.7 Use of Ultrasound

The use of ultrasound with ZVI has been found to enhance the rate of carbon tetrachloride degradation compared to ZVI alone. In such a system there are two ways in which carbon tetrachloride is degraded; pyrolysis inside bubbles produced by ultrasound and reduction on the ZVI surface.[32] Pyrolysis occurs due to the high temperatures (up to 5000K) from the localised adiabatic heating that accompanies the release of large amounts of energy during the sudden implosion of cavities formed from ultrasound. Compounds formed during pyrolysis are C_2Cl_6 and C_2Cl_4, these have been observed as intermediates in the ZVI/ultrasound system along with the $CHCl_3$ product from reduction by ZVI.[32]

In addition to the two separate mechanisms that degrade carbon tetrachloride the rate of carbon tetrachloride degradation is increased synergistically as well. This was seen in the 40-fold enhancement of the degradation due to the ZVI component in the presence of ultrasound. This is possibly due to the continuous ultrasonic cleaning of the surface, the enhanced rate of mass transport due to turbulent effects, a lower pH (due to the production of hydrochloric acid) and the increased surface area created by rupturing of particles. Iron corrosion is accelerated by ultrasound thus enhancing the reductive dehalogenation of carbon tetrachloride.

According to Hung and Hoffman in an aqueous system there are two other possible mechanisms in which ultrasonic action can degrade organic compounds; supercritical water reactions and hydroxyl radical reactions. Hydroxyl radicals are formed by homolytic splitting of a water molecule that has been vapourised into a bubble. The major products from this mechanism would be $COCl_2$, CO_2 and HCl.[32]

3. Oxidative Mechanisms

Recent work by Joo et al was the first to investigate the oxidative mechanisms with which zero-valent particles can degrade organic compounds. Their study examined the use of ZVI to produce Fe^{2+} ions which then degrade organic compounds in a Fenton-based chemical reaction.[33] Section 3.3.2 describes this work in detail.

Previous works using ZVI to destroy organophosphorous compounds or similar pesticides have shown that fast degradation (40mins) occurs in buffered aqueous solutions but have not investigated the mechanisms or the end products.[34, 35] In the case of Ghauch et al they assumed the reaction was reductive.[35]

3.1 Fenton Reagent Chemistry

Fenton's reagent is a $Fe(II)/H_2O_2$ mixture that has strong oxidising properties against many organic compounds. The active species in this system is commonly thought to be the

hydroxyl radical. However, as early as 1932 Bray and Gorin [36] suggested that the reaction might proceed via:

$$H_2O_2 + Fe^{2+} \rightarrow FeO^{2+} + H_2O \qquad \qquad \ldots(3.1)$$
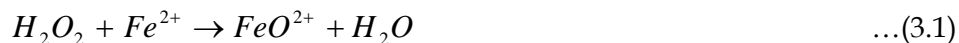
Recently there has been more debate as to whether hydroxyl radicals are actually produced or whether complexes of iron in higher than usual oxidation states are formed.[37, 38] Regardless of whether hydroxyl radicals or iron complexes are formed the products are the same.[39]

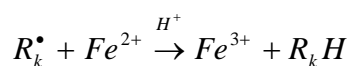The Fenton's reagent oxidation mechanism as described by Walling, is given in scheme 1a.[36]

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO\cdot$$

$$HO\cdot + Fe^{2+} \rightarrow Fe^{3+} + HO^-$$

$$HO\cdot + R_iH \rightarrow R_i^\bullet + H_2O$$

$$HO\cdot + R_jH \rightarrow R_j^\bullet + H_2O$$

$$HO\cdot + R_kH \rightarrow R_k^\bullet + H_2O$$

$$R_i^\bullet + Fe^{3+} \rightarrow Fe^{2+} + R_i^+$$

$$2R_j^\bullet \rightarrow DIMER\ product$$

$$R_k^\bullet + Fe^{2+} \xrightarrow{H^+} Fe^{3+} + R_kH$$
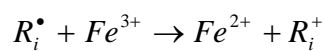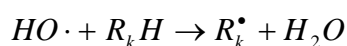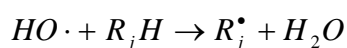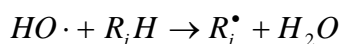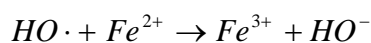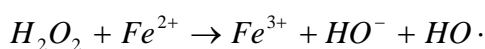
Scheme 1a[36]

In the case of unsaturated molecules addition may occur instead of hydrogen abstraction as shown in scheme 1b.

$$HO^\bullet + R_m{=}R_n \rightarrow HOR_mR_n^\bullet$$

$$HOR_mR_n^\bullet + Fe^{2+} \xrightarrow{\quad H^+ \quad} Fe^{3+} + HOR_mR_nH$$
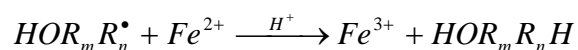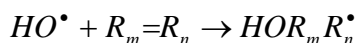
Scheme 1b

Competing processes include:

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \qquad \qquad \ldots(3.2)$$

$$2HO^\bullet \rightarrow H_2O_2 \qquad\qquad \ldots(3.3)$$

The perhydroxyl radical can then further react with iron species via the reactions:

$$HO_2^\bullet + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \qquad\qquad \ldots(3.4)$$

$$HO_2^\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \qquad\qquad \ldots(3.5)$$

The perhydroxyl radical can also be formed via:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \qquad\qquad \ldots(3.6)$$
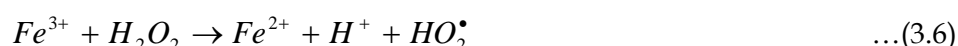
3.2 Hydroxyl Radical Chemistry

Different means of producing hydroxyl radicals have been utilised to destroy chemical and biological warfare agent simulants. Typical rates for the reactions of hydroxyl radicals with organic species are 10^9-10^{10} Lmol^{-1}s^{-1}, making them good prospects for warfare agent decontamination.

Gilleto et al describe the use of a Fenton-like reagent in their patented reactive decontamination formulation.[40] This patent claims that both CWA's and BWA's are degraded sufficiently to leave no toxic by-products. According to Giletto et al hydroxyl radicals will react non-selectively and rapidly with most CWA's.

3.2.1 Organophosphorous Compounds

Giletto et al found that diisopropyl methylphosphonate (DIMP, 0.2% remaining after 5mins) was least persistent of the diphosphonoesters while dimethyl methylphosphonate (DMMP, 0.9% remaining after 30mins) was the most persistent.[40] They suggest that the degradation of these simulants may occur via a S_N2 reaction (Scheme 2a) about the phosphorous atom releasing an oxygen centred ·OR radical. The order of the resulting radical stability is:

$$\cdot OCH(CH_3)_2 > \cdot OCH_2CH_3 > \cdot OCH_3$$

Thus the reaction of DIMP, which produces the most stable radical, will proceed fastest.
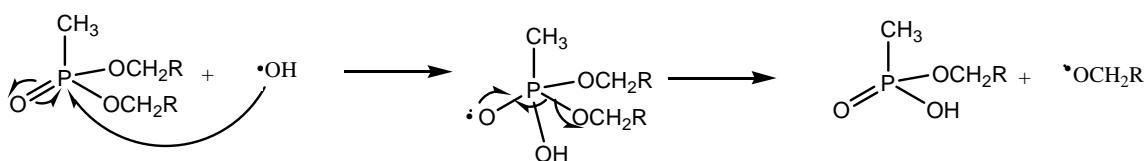
Scheme 2a

Aguila et al studied the mechanisms of hydroxyl radical reaction with methylphosphonates, using DMMP and diethyl methylphosphonate (DEMP).[41] Radiation was used in this study to create the reactive hydroxyl radicals. Similarly to Giletto et al[40] they found that DEMP (rate constant: $(6\pm1)\times10^8$ Lmol^{-1}s^{-1}) was degraded faster than DMMP (rate constant: $(2\pm1)\times10^8$ Lmol^{-1}s^{-1}).

By analysing the reaction products by ion chromatography Aguila et al determined that the reaction does not occur via the S_N2 reaction to release a ·OR radical. This reaction would result in the monoester (one substitution) or phosphonic acid (two substitutions) as products, viz., ethyl methylphosphonate (EMP)/methyl methylphosphonate (MMP) and/or methyl phosphonic acid (MPA). These are easily ionised; however no ionic products were found in the absence of oxygen.[41]

Two other possible mechanisms were proposed by Aguila et al; electron (e⁻) abstraction and ·H abstraction (scheme 2b). The first of these alternative mechanisms would produce a phosphorenyl radical but this was not observed experimentally. This species would be highly susceptible to nucleophilic addition of a water molecule and subsequent elimination of a ·OR group. This would result in an EMP/MMP reaction product, which, as already noted, was not present in the absence of oxygen.[41]

The ·H abstraction mechanism leads to a carbon-centred radical which then undergoes the Russell mechanism reaction and hydrolysis *in the presence of oxygen* to form MMP/EMP. Aguila et al provide further evidence for carbon-centred radicals by reacting tetranitromethane (TNM), known for its selective reactivity with carbon-centred radicals activated by α-oxygen or phosphorous functionalities, and observing adduct formation and TNM reduction.[41]

The eventual degradation products were identified as EMP/MMP, methylphosphonic acid and phosphate in the presence of oxygen. Oxygen is clearly beneficial for this decontamination process. The observed rates of reaction indicated a half-life of 15mins at an initial DMMP concentration of 2.65×10^{-4}M.[41]
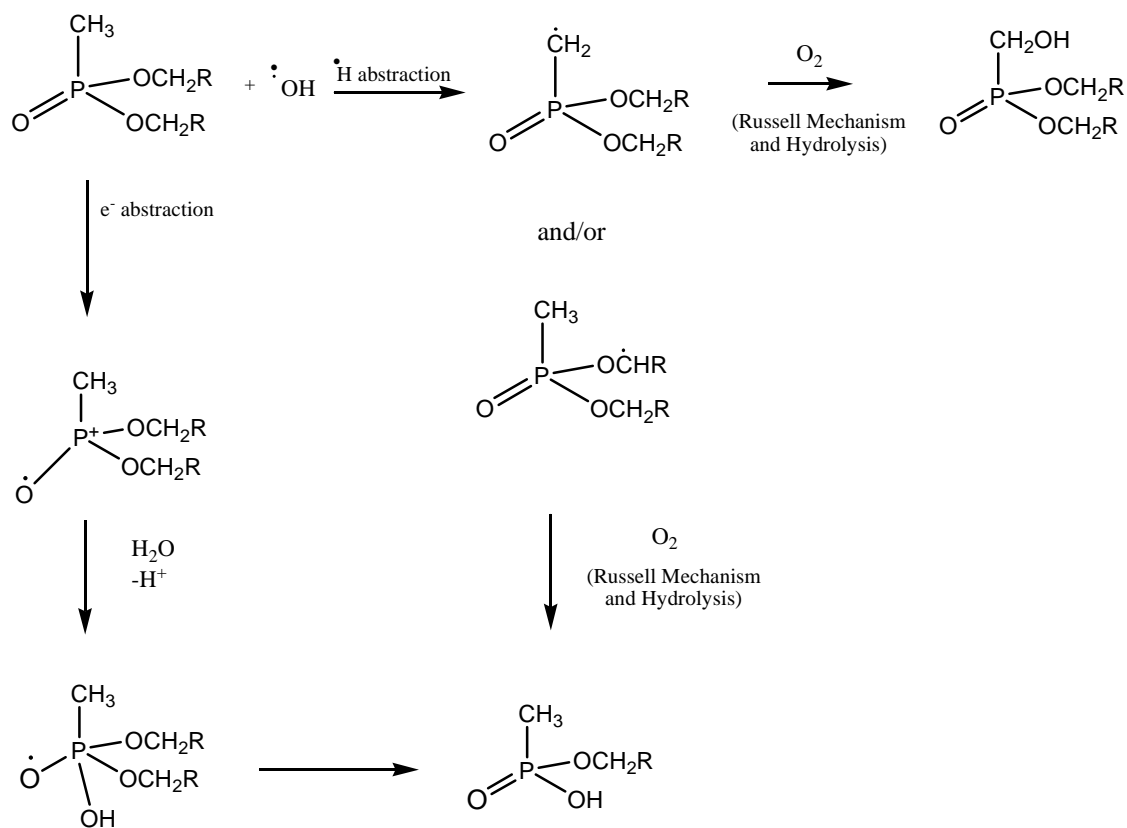
Scheme 2b

3.2.2 Sulfur-Containing Compounds

It is generally accepted that the reaction of hydroxyl radicals with dimethyl sulfide (DMS) proceeds via a two-channel mechanism, although there has been some contention over the formation of the adduct in reaction 3.8.[42] This two-channel mechanism accounts for the fact that there is a significant rate increase and a difference in products when performed in the presence of oxygen. Reaction 3.7 represents the oxygen-independent channel while reactions 3.8 and 3.9 represent the oxygen-dependent channel.

$$\cdot OH + CH_3 SCH_3 \rightarrow H_2O + CH_3 S \overset{\bullet}{C} H_2 \qquad \qquad \dots(3.7)$$

$$\cdot OH + CH_3 SCH_3 \Leftrightarrow CH_3 \overset{OH}{\underset{|}{S}} CH_3 \qquad \qquad \dots(3.8)$$

$$CH_3 \overset{OH}{\underset{|}{S}} CH_3 + O_2 \rightarrow products \qquad \qquad \dots(3.9)$$

The oxygen-independent pathway, reaction 3.7, proceeds via hydrogen abstraction. The free radical product then reportedly reacts with oxygen in the presence of NO_x according to scheme 3a,[43, 44] where M is a third body which may be involved in the reaction.[45]

$$\cdot OH + CH_3SCH_3 \rightarrow H_2O + CH_3S\overset{\bullet}{C}H_2$$

$$CH_3S\overset{\bullet}{C}H_2 + O_2 + M \rightarrow CH_3SCH_2O\overset{\bullet}{O} + M$$

$$CH_3SCH_2O\overset{\bullet}{O} + NO \rightarrow CH_3SCH_2\overset{\bullet}{O} + NO_2$$

$$CH_3SCH_2\overset{\bullet}{O} + M \rightarrow CH_3\overset{\bullet}{S} + CH_2O + M$$
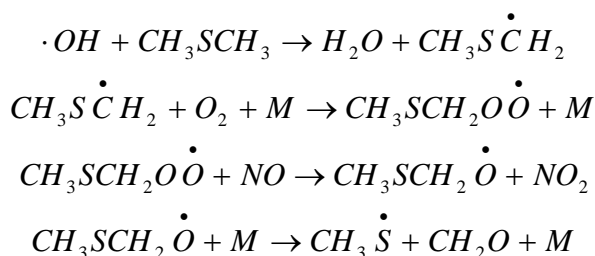
Scheme 3a

In the absence of NO_x the reaction proceeds according to scheme 3b in approximately equal yields:

$$CH_3SCH_2O\overset{\bullet}{O} + H\overset{\bullet}{O}_2 \rightarrow CH_3SCH_2OOH + O_2$$

$$\rightarrow CH_3SCHO + H_2O + O_2$$
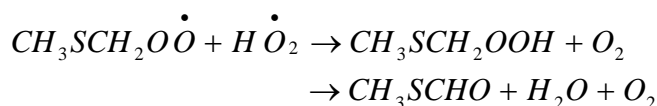
Scheme 3b

The $CH_3S\cdot$ radical eventually forms sulfur dioxide as the major sulfur-based product (80±10% of total sulfur content). Formaldehyde is the major carbon product accounting for 90±6% of the total carbon content.[43] Methyl sulphonic acid has been observed as a product in the presence of NO_x. In the absence of NO_x, carbonyl sulfide and methyl thioformate (MFT) have been observed, though MFT photo-oxidises rapidly. In the absence of NO_x, sulfur dioxide and dimethyl sulfoxide (DMSO) are the major sulfur products. Although DMSO mostly comes from the oxygen-dependent channel it has been observed in a nitrogen environment and it is possible that the $CH_3S\cdot$ reacts with the adduct from reaction 3.8 to form DMSO.[43]

It is clear from comparing Schemes 3a and 3b that the presence of NO_x significantly affects the products of the reaction of DMS with hydroxyl radicals. It also affects the kinetics of the reaction.[43]

A significant isotope effect in the absence of oxygen is evidence for the hydrogen abstraction method. The rate constant at 298K for DMS is reported as $(2.98\pm 0.2)\times10^9$ Lmol⁻¹s⁻¹, for DMS-$_{d6}$ it is reported as $(1.05 \pm 0.1)\times10^9$ Lmol⁻¹s⁻¹.[46]

The second channel for the hydroxyl radical reaction with DMS is via addition to and oxidation of the sulfur atom to form the adduct in reaction 3.8. This adduct is weakly bound with a bond strength of approximately 11 kcalmol⁻¹,[46] which means it is easily reversible. For this reason this pathway is oxygen dependent for, without oxygen,

equilibrium is quickly reached in the adduct formation reaction. In the presence of oxygen the adduct is removed thus allowing more adduct to be formed and removed and thus the reaction to proceed via this pathway.

The major end product of the reaction of oxygen with the adduct is DMSO (3.10) with a reported branching ratio of 0.5.[44] The DMSO can then possibly be oxidised further to form dimethylsulphone (DMSO$_2$).

$$CH_3 \overset{\overset{OH}{|}}{S} CH_3 + O_2 \rightarrow H \overset{\bullet}{O}_2 + CH_3 \overset{\overset{O}{||}}{S} CH_3 \qquad \qquad \dots (3.10)$$
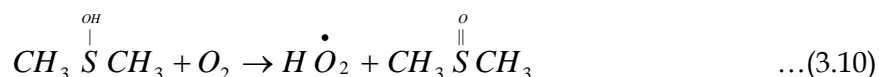
Urbanski et al found that hydroxyl radicals reacted with DMSO but not via the hydrogen abstraction mechanism. The hydrogen abstraction method was deemed not to be a significant pathway, as there appeared to be no kinetic isotope effect. DMSO, DMSO$_2$ and methyl sulphonic acid (MSA - CH_3SO_3H) were the major products of hydroxyl radical reaction with dimethyl sulfide in the presence of oxygen.[47] MSA only occurred in the presence of NO$_x$.[48]

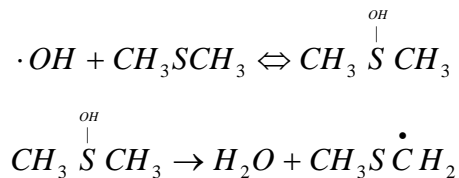There has been some debate over the existence of the hydroxyl radical-DMS adduct. This is due to the very weak bond between the hydroxyl group and the sulfur. One research group, Gu and Tureck [as referenced in 42, 46] claim, based on theoretical and experimental studies, that the adduct is unstable and in fact is not a bound species. However McKee [as referenced in 42, 46] also performed theoretical studies and found the adduct had a binding energy of 6.0kcal mol^{-1} and that this was possibly underestimated by about 4kcal mol^{-1}. If so this compares well, given the errors associated with the experimental observations, to other measured values of the enthalpy of adduct formation: -10.3±2.5 kcal mol^{-1} [46] and -13.0±3.3 kcal mol^{-1}.[42]

Both Hynes et al and Barone et al raised questions about the experimental results obtained by Gu and Tureck.[42, 46] Both note that the experimental procedure leads to highly excited products, which, even though they may be stable, are subject to rapid decomposition. This makes this method unsuitable for determining the binding energy of weakly bound species. Hynes et al also claim that Gu and Tureck have mistakenly interpreted the mechanism as formation of the adduct, which then dissociates to form products. However, experimental observations of oxygen dependency indicate that the adduct either reacts with oxygen or dissociates back into reactants.

It is possible to explain the different products and increased rate in the presence of oxygen by assuming that the hydrogen abstraction occurs via the mechanism in Scheme 4. However if the reaction was to proceed via Scheme 4 then it would be expected that in excess oxygen the rate constants for DMS and DMS-$_{d6}$ would be the same. This is because Reaction 3.9 would proceed in preference to the second reaction in scheme 4, assuming that there is no isotope effect in Reaction 3.9.[46] However Barone et al found that the difference between the rates of reaction was the same in the presence of oxygen as it was

in the absence of oxygen.[46] This indicates that there are indeed two separate reaction paths.

$$\cdot OH + CH_3SCH_3 \Leftrightarrow CH_3 \overset{\overset{OH}{|}}{S} CH_3$$

$$CH_3 \overset{\overset{OH}{|}}{S} CH_3 \rightarrow H_2O + CH_3 S \overset{\bullet}{C} H_2$$

Scheme 4

Although the adduct channel has been demonstrated to occur, the observation by Turnipseed et al that at 298K replacing a nitrogen environment with oxygen does not significantly increase the rate coefficient indicates that at higher temperatures the adduct pathway is not significant.[44] In fact, according to Barone et al, adduct formation is minimal at temperatures above 258K.[46] Similar observations have been made by other researchers.[47, 49] This means that for all practical decontamination purposes we can assume that hydrogen abstraction is the dominant pathway.

Hynes et al reported that the adduct equilibrium (3.8) has a dramatic negative temperature dependency in the presence of oxygen or 1 atm of air.[42] Barone et al also noted that the reverse reaction rate increased with temperature while the forward reaction rate decreased slightly. Barone et al also found that the adduct reaction with oxygen was virtually independent of temperature over the temperature range used, although they stated that there was probably a slight temperature dependence. They also found that the reaction of DMS with hydroxyl radicals to form products other than the adduct was positively dependent on temperature at temperatures above 260K (where adduct formation is almost negligible). Below this temperature their experimental set-up led to non-Arrhenius behaviour.[46]

In Atkinson's review of gas phase hydroxyl radical chemistry he states that the rate constants for the hydroxyl radical reaction with sulfides increases with size of the straight chain alkyl substituent in the order of $CH_3CH_2SCH_2CH_3 > CH_3CH_2SCH_3 > CH_3SCH_3$.[49] The rate constant (k) for the reaction of DMS was 3.8×10^9 Lmol^{-1}s^{-1} under atmospheric conditions. It was observed that the rates of reaction increased with increasing oxygen concentration. For di-*t*-butyl sulfide non-Arrhenius behaviour was noted. This observed non-Arrhenius relationship of the t-butyl substituents could be due to a changing ratio of sulfide that reacts via hydrogen abstraction and radical addition at approximately 298K.[49]

Disulfide products observed from the reaction of hydroxyl radicals with thiols indicates that CH$_3$S$\cdot$ radicals can also combine, even in the presence of air. The rates of hydroxyl addition were found to correlate with the ionisation potential of the compound, while the rates of reactions proceeding via hydrogen abstraction correlated with C-H bond dissociation energies.[49]

Giletto et al tested their patented system's effectiveness against chloroethylethyl-sulfide (CEES) as a simulant for mustard. They found that Oxone® (see Section 3.3.1) alone destroyed CEES much faster (100% in 3mins) than both the activated/catalysed system (37% in 3mins) and the mixture of the two (10% oxone → 69% in 3mins). However oxone on its own produced chloroethylethyl sulfone as the degradation product, which corresponds to the production of the highly toxic bis(2-chloroethyl) sulfone in the case of mustard. The mixture produced very little of this compound and thus is the more preferable decontaminant. CEES destruction was also studied with a gel version of the decontaminating system. It was found that destruction occurred more slowly in this system (at 3mins 31% remaining versus 67%). This suggests that the rate of reaction is inversely proportional to the viscosity indicating that the reaction may be diffusion controlled.[40]

Demeton-S and Malathion (Figure 3.1) were used as VX simulants in the patent by Giletto et al. Dem-S, which resembles VX at the P atom, was not detected after 3mins. It was stated that the sulfur in the hydrophobic chain was the first to be oxidised followed by the sulfur next to the phosphorous. Malathion was persistent beyond 90mins even with a thousand times excess of oxidant. It was thought that this was due to its poor solubility. Use of FC-99 surfactant enhanced the degradation from 15% to 80% in 20mins. Inclusion of the oxone increased all rates of reactions.[40]
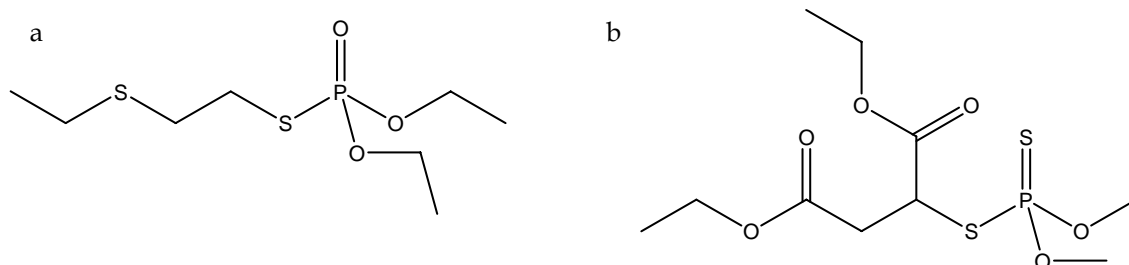
Figure 3.1: a) Demeton-S and b) Malathion

Weres and Pocekay investigated the destruction of chemical agent simulants by hydroxyl radicals produced from hydrogen peroxide.[50] Using a 50% H_2O_2/H_2O solution they produced hydroxyl radicals by both UV light and catalytic surfaces:

$$H_2O_2 \xrightarrow{UV} 2 \cdot OH \qquad \qquad \dots(3.11)$$

While hydrogen peroxide reacts directly with some chemical agents, hydroxyl radicals react non-selectively with virtually all chemical agents as they can strip any aliphatic H atom:

$$RH + \cdot OH \rightarrow R \cdot + H_2O \quad \Delta H \approx -23 \, to - 30 kcal, \quad \Delta S \approx 0 \qquad \dots(3.12)$$
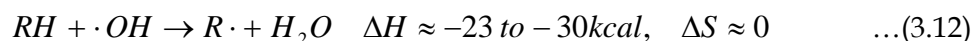
However any reduced sulfur compounds may be preferentially attacked at the sulfur atom.

The $R\cdot$ radical released by the hydroxyl radical hydrogen abstraction will then react with oxygen or H_2O_2, releasing more radicals to react with the agent in a chain reaction. This means that degradation in a H_2O_2/H_2O system is rapid and that the rate-limiting factor in the reaction is the mass transfer kinetics, in particular the rate of solution. In other words, the more soluble an agent is, the faster it will be degraded. This effect was observed by Gilleto et al (2003) with Malathion where the addition of surfactant increased its solubility and also its rate of degradation. It was found that UV light worked better than the catalytic metal oxide/sulfide surfaces at degrading agent simulants, presumably by producing more hydroxyl radicals.[50]

3.3 Decontamination Based on Fenton's Reagent

The effectiveness of photo-assisted Fenton based systems degrading organophosphorous pesticides in oxygenated solutions was studied by Doong and Chang.[51] They found that Fenton's reagent was an improvement on the UV/hydrogen peroxide system alone. A ZVI/hydrogen peroxide/UV system was also studied and found to be as effective as the Fenton's reagent.[51]

In 1992 Leslie and Ward published work based on Fenton reagent chemistry. They studied the use of oxone/metal ion systems for destroying DIMP and found that while Cr(III), Mn(II) and Co(II) enhanced the destruction of DIMP, Fe(II) and Ag(I) did not.[39]

Also in 1992 Yang et al claimed that, up to that time, no iron Fenton based catalysts were effective against HD and VX. A possible reason given for this was that the decomposition of the peroxide by the iron produced molecular oxygen that was then leaving the reaction mixture and deactivating the catalyst.[52]

3.3.1 Use of Oxone with Fenton's Reagent

In 2003 Gilleto et al obtained a patent for a reactive decontaminant gel. The claims of this patent are described more fully in sections 3.2.1 and 3.2.2. Importantly the patent describes the destruction of simulants for HD and VX.[40]

Gilleto et al's system involved the use of at least one oxidant, a source of phosphate ions, an activating species and an inert sorbent material in an aqueous solution. The oxidants in their specific formulation are hydrogen peroxide and oxone, and ferrous salts/ions are the activating species. Oxone® (a Dupont product) is a crystalline powder mixture of formula $2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$, and its active ingredient is the monopersulfate ions. The hydrogen peroxide/oxone combination was useful in this formulation as the effectiveness

against biological agents is increased relative to either oxidant alone. Gilleto et al suggested that this was due to the hydrogen peroxide being able to penetrate the spore coat thus allowing oxone greater access than it had on its own.[40]
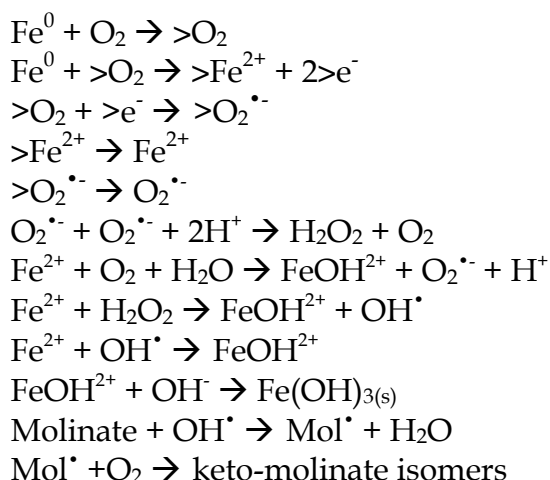
The addition of oxone to a normal Fenton reagent aids in the decontamination, as the phosphate ions are a good masking agent for ferric ions and so slow the release of ferrous ions. This limitation of the immediate availability of iron means there is a more continuous source of the ferrous ions. This in turn maintains the production of hydroxyl radicals at a steady rate. Phosphate ions also stabilise the hydrogen peroxide and control the temperature of the exothermic reaction.[40]

3.3.2 ZVI and Oxygen as Alternative Starting Reagents

Joo et al studied the degradation of the pesticide Molinate solutions using nanoparticulate ZVI suspensions of average particle size 50nm. Molinate degradation by ZVI was studied in deoxygenated conditions, in the presence of air and in 100% oxygen environments. The presence and amount of oxygen was vital to the degradation. Scheme 5 shows the mechanism proposed to explain their observations. Surface species are represented by the symbol '>' and the mechanism assumes a pH>4.8 meaning that the superoxide radical is deprotonated.[33]

Although hydrogen peroxide is not added to the system it is produced by the reaction of superoxide radicals and protons. Combined with the oxygen-induced oxidation of ZVI to form ferrous ions this sets up the Fenton chemistry responsible for the degradation of Molinate. The major advantage of this system over an ordinary Fenton system is that while normally the reaction stops once all the added ferrous ions are used the ZVI provides a constant source of the ions and hydrogen peroxide. However this reaction, and in particular the production of hydrogen peroxide, is limited by the solubility of oxygen in water.[33]

The pH of the solution is an important factor in the degradation, the rate of which is slightly faster at pH 4 than at pH 8.1. Also degradation continues at pH 4 while at pH 8.1 the degradation rate slows down and seems to plateau. This is consistent with the proposed mechanism (Scheme 5) in that the production of hydrogen peroxide at pH 8.1 is initially smaller than that at pH 4 and decreases to nothing at about the time the degradation plateaus.[33]

$$Fe^0 + O_2 \rightarrow >O_2$$
$$Fe^0 + >O_2 \rightarrow >Fe^{2+} + 2>e^-$$
$$>O_2 + >e^- \rightarrow >O_2^{\bullet-}$$
$$>Fe^{2+} \rightarrow Fe^{2+}$$
$$>O_2^{\bullet-} \rightarrow O_2^{\bullet-}$$
$$O_2^{\bullet-} + O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2$$
$$Fe^{2+} + O_2 + H_2O \rightarrow FeOH^{2+} + O_2^{\bullet-} + H^+$$
$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + OH^\bullet$$
$$Fe^{2+} + OH^\bullet \rightarrow FeOH^{2+}$$
$$FeOH^{2+} + OH^- \rightarrow Fe(OH)_{3(s)}$$
$$Molinate + OH^\bullet \rightarrow Mol^\bullet + H_2O$$
$$Mol^\bullet + O_2 \rightarrow keto\text{-}molinate\ isomers$$

Scheme 5[33]

3.3.3 ZVI Reduction as an Enhancement to Fenton Reagent Oxidation

For contaminants that are difficult to either oxidise or reduce a combination of ZVI reduction and Fenton reagent oxidation may be useful. So far studies on these combined processes have been focused on the explosives TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). These compounds were studied because, while they can be reduced by ZVI, they are not completely broken down,[53] nor can they be effectively oxidised due to hindrance by the nitro groups.[54] However, the reduction products of TNT and RDX, such as triaminotoluene, can be oxidised readily.

The studies by Oh et al showed that combining these two treatments increased the degradation of TNT by approximately 20% and RDX by approximately 60% compared to that of Fenton reagent treatment alone. Both compounds showed an overall removal of approximately 96% in about 90mins, with 92.2% and 79.3% nitrogen recovered as NH_4^+ and NO_3^- for TNT and RDX respectively.[54]

In contrast to Oh et al, Krishna et al used Fenton reagent pre-treatment followed by ZVI reduction to remove arsenic. This order was chosen as ZVI treatment worked well for arsenic (V) (90% removal) but not for arsenic (III) (50% removal); thus by firstly oxidising arsenic (III) to arsenic (IV) all arsenic can be effectively removed by ZVI. Fenton's reagent was used as the oxidising mechanism and this combination resulted in a removal of arsenic (III) from 2.5mg/l to 10ppb.[55]

3.3.4 Use of Cyclodextrins with Fenton's Reagent

In-situ soil remediation techniques based on Fenton's reagent tend to be inefficient as they involve species that are highly reactive with certain components of the soil. They have the tendency to hold the iron and pollutant in separate 'microenvironments', thereby preventing them from coming into contact. Only with high H_2O_2 concentrations do the pollutants become desorbed.[56]

Lindsey et al examined the effect of cyclodextrins (CDs) on the rate of degradation of organic compounds by Fenton's reagent. Cyclodextrins are torus shaped molecules with a hydrophobic interior and hydrophilic exterior. Thus they are useful for enhancing the aqueous solubility of hydrophobic compounds. They can also complex with both metals and hydrophobic organic molecules, thereby holding the metal catalyst and pollutant in close proximity and increasing the chance of contact and thus the rate of reaction. Therefore CDs should enhance the rate of pollutant degradation via this iron-cyclodextrin-pollutant complex. These complexes have been identified by electrospray-MS and indicated by absorbance spectra. The variety of cyclodextrins available may also allow the targeting of compounds of certain molecular sizes, thus increasing the specificity of the reaction.[56]

As mentioned in Section 2.6, Bizzigotti et al found that the use of CDs actually decreased the rate of reductive degradation of PCE with ZVI. This was due to separation of the contaminant from the iron surface where the degradation occurs.[31] In oxidative Fenton reagent based degradation, like that in section 3.3.2, the application of CDs may prove effective, as the actual degradation reaction does not occur on the ZVI surface (see Scheme 5).

Additions of CDs to Fenton systems with low iron concentrations were found to decrease the rate of degradation. With increased iron content the rate of reaction increased. At higher iron concentrations the majority of CDs bound with pollutant would also have had iron bound to them. At lower iron concentrations many pollutants would not have had iron bound to their CDs and thus, effectively, would have been isolated from any hydroxyl radicals. The decrease in reaction rate for each pollutant varied with size. The larger the pollutant molecule, the lower the degree of inclusion into the interior of the CD and the so the smaller the decrease in reaction rate. This indicated that the hydroxyl radical scavenging by CD is negligible as was expected.[56]

In the case of polychlorinated biphenyls (PCBs) there was a significant increase in the rate of degradation despite the fact that the CD scavenging rate is much faster than the reaction rate between hydroxyl radicals and PCBs. This strongly suggests that the advantages gained from this system are due to the ternary complexes. Sonication was found to increase the speed of equilibration of PCBs with CD.[56]

Hydroxyl radical formation at Fe-CD-pollutant complexes favours the degradation of pollutant over the reaction with bulk scavengers due to the close proximity of the radical

to the pollutant. Increasing the scavenger amount causes the rate of degradation to decrease when there is no CD present. In the presence of CD however there is no effect on the rate of degradation. This indicates that in 'dirty' matrices a more dramatic effect may be seen as the effect of hydroxyl radical scavengers is negated.[56]

An alternative explanation for the increased rate of degradation in the presence of CD is that Fe-CD complexing increases the amount of hydroxyl radicals formed. However, this does not explain the decreased rates of reaction at low iron concentrations. Also the measured concentration of hydrogen peroxide decreases at a slower rate when CD is present, leading to a lower bulk concentration of hydroxyl radicals.[56]

A possible concern with the use of cyclodextrins is that they may alter the products formed. For example when the degradation of phenol was studied it was found that the ratio of catechol to hydroquinone changed with extent of reaction but was increased significantly by the presence of CD.[56]

The CD complexes also enable the degradation reaction to occur at higher pHs. Normally, low pH is required for iron solubility, but iron chelation allows reaction to take place at near neutral pHs.[56]

4. Nanoscale ZVMs

The use of nanoparticles is of interest primarily due to their large surface area. As stated in Section 2.2 the most important factor in the determination of dechlorination rate is the iron surface area concentration.[9] The observed rate constant, k_{obs}, is directly proportional to ρ_a, where ρ_a is the surface area concentration (surface area × mass concentration) and the proportionality constant is the specific reaction rate constant k_{SA} ($Lh^{-1}m^{-2}$).[17]

Johnson et al looked at iron surface areas, ranging from $0.0567 m^2/g$ to $3.3 m^2/g$, and found that k_{obs} was proportional to ρ_a.[17] This does not extend from the microscale to the nanoscale particle range, however. In addition to having an increased surface area nanoscale metal particles have high surface energies and thus are even more reactive than would be expected from just the increase in surface area.[23] Nanoscale particles are perhaps also easier to suspend in solution and thus aid transport and diffusion processes.[26]

Wang and Zhang found that the surface-area-normalised rate constants for the nanoscale iron particles were approximately three times those of the commercial, microscale, iron particles.[23] Lien and Zhang found that surface-area-normalised reactivities for their nanoparticles were one or two orders of magnitude higher than those reported for commercial grade irons.[26] Care must be taken with Lien and Zhang's comparisons as

factors such as iron pre-treatment (that is, surface cleanliness [15]) and others can have a large effect on reactivities.

Nanoscale particles can be readily incorporated onto/into various supports, thus widening their scope of applications.[23] According to Ponder resin-supported nanoscale iron performed as well as non-supported nanoscale iron (90% of Cr(VI) and Pb(II) degraded in 48hrs).[3]

Nanoscale metal particles need to be stabilised, to prevent both coalescence and possible oxidation. Metal clusters are most commonly stabilised by ligands during synthesis. The choice of ligand will determine the solubility of the metal nanoparticles and one ligand may be exchanged for another in order to tailor the particles to a particular solvent. For example gold clusters can be made soluble in dichloromethane, water and pentane with $(PPh_3)_{12}Cl_6$, $(BSH)_{12}{}^{24-}$ and $(T_8\text{-OSS-SH})_{12}Cl_6$ ligands respectively. The later two ligands can be attached via ligand exchange reactions with the first ligand.[57]

Schrick et al has suggested that the background corrosion of iron will limit the lifetime of zero-valent nanoparticles compared to larger iron particles.[25] According to Lien and Zhang the nanoscale iron particle reactivity decreases substantially after a few days of air exposure.[26]

5. Methods of Incorporating ZVI Particles

5.1 Solid Supports

Solid supports such as zeolites, silica and activated carbon can be used to anchor nanoscale particles.[24]

Ponder et al found that the material used to support nanoscale iron had a strong effect on reaction rates despite being inert to redox reactions. It was suggested that this was due to the evenness of the dispersion on the support surface and the surface roughness, which affects specific loading. Use of high surface area supports was found to reduce soluble metal ions much faster than unsupported zero-valent iron.[58]

These studies were done with 10-30nm ZVI particles (prepared by borohydride reduction) impregnated onto support materials, which included silica, polymeric resins and metal oxide powders (eg ZrO_2). The silica gel and polymeric resins were found to be unstable in highly alkaline environments. Poorly crystalline ZrO_2 was found to be the best support for removal of pertechneate in a highly alkaline environment. Silica and polymeric resin 'ferragel' supports were found to significantly increase the reaction rate of chromate reduction.[58]

Stable colloidal dispersions of zero-valent iron (50-150Å) can be prepared by thermally decomposing $Fe(CO)_5$ in dilute solutions of functional polymers. The polymer appears to act as a catalyst for this thermal decomposition and induces particle nucleation. However these colloidal dispersions are subject to oxidation by air.[59] This type of 'in-situ growth' is the result of an interaction between the metal compound and the polymer matrix. Either the metal can be coordinated directly to the polymer (via a pendant-polymer amino or hydroxyl group) or an unsaturated group in the polymer can be substituted for a ligand in the metal complex during thermolysis. The reaction conditions in these processes determine the size of the metal nanoparticles. Additionally the size is inversely proportional to the polarity of the polymer groups. A similar material can be obtained by reducing metal salts from polymer solutions or suspensions.[60]

Nanoscale particles can be incorporated into a polymer shell by emulsion polymerisation where the monomer is adsorbed onto the surface. This requires nanoscale particles in the first place and would hinder access to the particles unless the shell was highly porous.[60]

5.2 Dendrimers

Dendrimers are well-defined spherical shaped nanoreactors that possess the structure and ligand sites (dendrimer functional groups) that enable the organisation of the metal particles. This organisation arises from the particles being fixed within the interior due to physical restraints of the highly branched dendrimer, and chemical interactions.[61]

A dendrimer is built from branched molecules, which gives it its spherical shape. It has a core to which multi-functional (functionality of 3 or more) molecules ('dendrimer parts') are attached to form the 1st generation. Subsequent multi-functional molecules can be attached to form the desired number of generations. As an example the poly(amidoamine) (PAMAM) dendrimer in Balogh and Tomalia [61] is shown in figure 5.1.
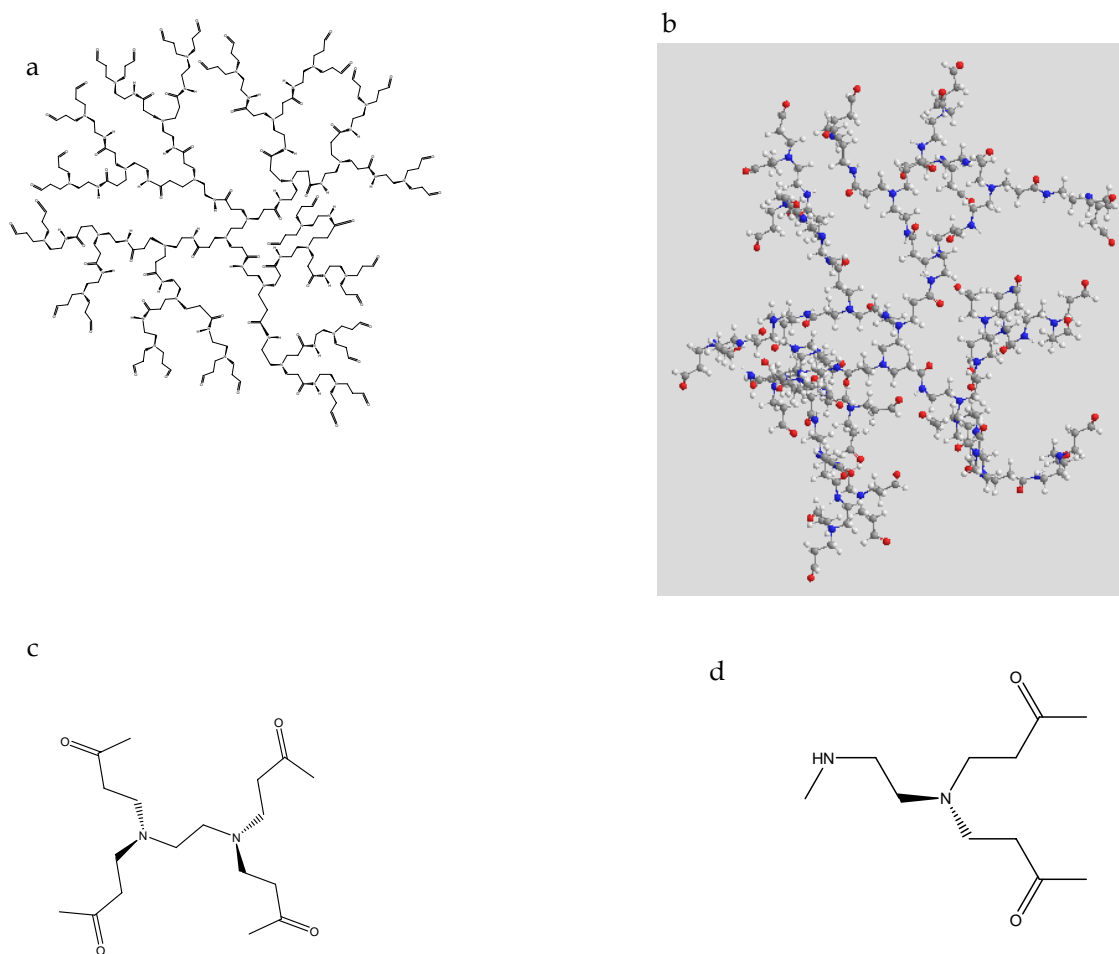
Figure 5.1 PAMAM Dendrimer a) 3rd generation dendrimer, b) 3D 'ball and stick' model of 3rd generation dendrimer c) dendrimer core and d) the dendrimer branching groups

A metal can be incorporated into a dendrimer if the metal (introduced as an ion) is suitably soluble in the dendrimer. This solubility is determined by the surface properties of the dendrimer functional groups. For example with PAMAM (poly(amidoamine)) and Cu(II) ions the copper complexes with the amidoamine groups.[61]

Once the metal ion is complexed to the dendrimer it can either be reacted to complex with new ligands or reduced to form the zero-valent metal. Balogh and Tomalia showed that while copper nanoclusters prepared conventionally tended to aggregate rather quickly, by incorporating the copper(II) ions into the dendrimer and subsequently reducing it with hydrazine to Cu(0), the Cu(0) remained unaggregated for more than 90days in the absence of oxygen. However exposure to atmospheric oxygen caused oxidation to Cu(II) complexes.[61]

While the internal dendrimer branching groups determine the solubility of the metal in the dendrimer, the end-groups of the dendrimer control the macro-solubility in solvents.[62] This means that a metal insoluble in a particular solvent can be made soluble in that solvent by incorporating it into a dendrimer with the right end-group chemistry.

The in-situ exchange of one dendrimer-encapsulated metal for another is also possible via a redox reaction provided the metal being replaced is capable of reducing the metal replacing it (i.e. is less noble). For example Cu can be replaced by Ag, Au, Pt or Pd. This method can be used to produce bi- and tri-metallic species.[62] The process involves firstly incorporating the metal ion into the dendrimer and reducing it to the zero-valent state. The more noble metal is then introduced in an ionic or complexed form, which then oxidises the first metal by reducing to its zero-valent state. Data indicate that these exchange reactions go to completion.[62]

This intradendritic exchange of metal particles is useful as the metal ion incorporated into the dendrimer must be able to form strong complexes or covalent bonds with the interior functional groups. If a metal ion cannot form strong enough bonds to the dendrimer it can possibly exchange with one that can. Many metal ions do not partition well enough to form stable composites.[62]

Zhao and Crooks found that their intradendrimer particles had diameters less than 4nm. (Their reported dendrimer diameter was 6.7nm) They also found that encapsulated Ag was very stable with no precipitation observed even after storage for more than 2 months in air, strongly suggesting that the Ag nanoparticles were encapsulated within the dendrimer.[62]

These Ag nanoparticles had an average size of 2.8nm (c.f. 15nm by direct reduction). The theoretical value was 1.5nm. Pt particles prepared this way were 1.4nm, very close to theoretical 1.2nm, while Au particles were 2.3nm compared to a theoretical value of 1.1nm.

Dendrimer encapsulated metal nanoparticles can be used for homogeneous and heterogenous catalysis indicating that (i) the substrates can enter the dendrimer interior and undergo reactions and (ii) the metal nanoparticles are not fully passivated.[62]

The problem with this method for producing ZVI is that iron has a negative redox potential and cannot replace copper or many other metals. A strong reducing agent capable of reducing an iron complex would be required.

6. Challenges to the Application of ZVI Nanoparticles

During investigations of the potential of ZVI to reductively decontaminate compounds a few challenges to its practical application have arisen. The first is that the reactivity of iron decreases with time possibly due to formation of metal hydroxides or carbonates that partially passivate the surface. Secondly the iron surface loses reactivity on exposure to air as it is oxidised by atmospheric oxygen. This oxidation is exaggerated when nanoscale particles are used (see Section 4).

Another limitation, in terms of chlorinated hydrocarbons, is that the iron reactivity decreases with the degree of halogenation resulting in an accumulation of these compounds, eg vinyl chloride, which have toxicological implications.[22, 23]

Various methods have been used to try and overcome these challenges.[22] These include ultrasound (see Section 2.8),[32] bimetallic species (Section 2.6) and use of external voltage [Cheng and Wu, 1998 as referenced in 22].

7. Conclusions and Recommendations

While there are significant challenges to be faced, the use of zero-valent metals as a means of degradation shows promise. The use of bimetallic particles has shown that problems such as toxic by-products and decreased reactivity can be significantly reduced, if not eliminated. Also the use of ultrasound can help overcome problems associated with contamination of the iron surface.

Besides increased reactivity, nanoscale particles have the additional advantage of being relatively easily incorporated into support structures, potentially without altering their reactivity significantly. This broadens their potential applications.

Due to the necessity to degrade organophosphorous compounds we must look at oxidative mechanisms of degradation. Thus the application of ZVI to Fenton reagent chemistry, while in the early stages of development, is extremely promising and worth further examination. The problems faced here are similar to those in reductive mechanisms – mainly the loss of reactivity of the iron on exposure to the atmosphere and toxic by-products.

In summary, the literature reviewed for this report has shown that nanoscale zero-valent metal particles have the potential to be used as a decontaminant against chemical warfare agents. The incentive to DSTO to explore these materials for application against chemical warfare agents is their demonstrated reactivity and the possibility of increasing their selectivity. Of particular interest will be the application of n-ZVI particles in the form of a

spray for use on different surfaces. Possible future directions should also include investigating bimetallic particles and the use of various delivery systems for n-ZVI particles.

8. References

1. Choe, S., Chang, Y.-Y., Hwang, K.-Y., and Khim, J., 'Kinetics of Reductive Denitrification by Nanoscale Zero-Valent Iron'. *Chemosphere*, 2000, **41** (8) pp. 1307-1311.

2. Ponder, S.M., Darab, J.G., and Mallouk, T.E., 'Remediation of Cr(VI) and Pb(II) Aqueous Solutions Using Supported, Nanoscale Zero-valent Iron.' *Environmental Science and Technology*, 2000, **34** (12) pp. 2564-2569.

3. Ponder, S.M., Darab, J.G., Bucher, J., Caulder, D., Craig, I., Davis, L., Edelstein, N., Lukens, W., Nitsche, H., Rao, L., Shuh, D.K., and Mallouk, T.E., 'Surface Chemistry and Electrochemistry of Supported Zerovalent Iron Nanoparticles in the Remediation of Aqueous Metal Contaminants'. *Chemistry of Materials*, 2001, **13** pp. 479-486.

4. Ghauch, A., and Suptil, J.,, 'Remediation of S-Triazines Contaminated Water in a Laboratory Scale Apparatus using Zero-Valent Iron Powder'. *Chemosphere*, 2000, **41** pp. 1835-1843.

5. Singh, J., Comfort, S.D., and Shea, P.J., 'Iron-Mediated Remediation of RDX-Contaminated Water and Soil under Controlled Eh/pH.' *Environmental Science and Technology*, 1999, **33** (9) pp. 1488-1494.

6. Moore, A.M., De Leon, C.H., and Young, T.M., 'Rate and Extent of Aqueous Perchlorate Removal by Iron Surfaces'. *Environmental Science and Technology*, 2003, **37** (14) pp. 3189-3198.

7. Tratnyek, P.G., Scherer, M.M., Johnson, T.L., and Matheson, L.J. 'Permeable Reactive Barriers of Iron and Other Zero-Valent Metals', IN: *Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications* (Ed, M.A. Tarr) 2002, Marcel Dekker, Inc, New York, pp. 371-421.

8. Doong, R.-A., Chen, K.-T., Tsai, H.-C.,, 'Reductive Dechlorination of Carbon Tetrachloride and Tetrachloroethylene by Zerovalent Silicon-Iron Reductants'. *Environmental Science and Technology*, 2003, **37** (11) pp. 2575-2581.

9. Matheson, L.J. and Tratnyek, P.G., 'Reductive Dehalogenation of Chlorinated Methanes by Iron Metal'. *Environmental Science and Technology*, 1994, **28** (12) pp. 2045-2053.

10. Arnold, W.A., Ball, W.P., Roberts, A.L., 'Polychlorinated Ethane Reaction with Zero-Valent Zinc: Pathways and Rate Control'. *Journal of Contaminant Hydrology*, 1999, **40** (2) pp. 183 - 200.

11. Arnold, W.A. and Roberts, A.L., 'Pathways of Chlorinated Ethylene and Chlorinated Acetylene Reaction with Zn(0).' *Environmental Science and Technology*, 1998, **32** (19) pp. 3017-3025.

12. Roberts, A.L., Totten, L.A., Arnold, W.A., Burris, D.R., and Campbell, T.J., 'Reductive Elimination of Chlorinated Ethylenes by Zero-Valent Metals'. *Environmental Science and Technology*, 1996, **30** (8) pp. 2654-2659.

13. Roberts, A.L., Arnold, W.A., Jans, U., Totten, L.A., and Fennelly, J.P., *Mechanistic Investigations of Zero-Valent Metal Reactions with Organohalides*, Report no: AD-A378793 AFRL-ML-TY-TR-1999-4556. 1999, Baltimore. University of Iowa, Johns Hopkins Univ.

14. Sayles, G.D., You, G., Wang, M., and Kupferle, M.J., 'DDT, DDD, and DDE Dechlorination by Zero-Valent Iron.' *Environmental Science and Technology*, 1997, **31** (12) pp. 3448-3454.

15. Chen, J.L., Al-Abed, S.R., Ryan, J.A., and Li, Z., 'Effects of pH on Dechlorination of Trichloroethylene by Zero-Valent Iron.' *Journal of Hazardous Materials*, 2001, **83** (3) pp. 243-254.

16. Wust, W.F., Kober, R., Schlicker, O., and Dahmke, A., 'Combined Zero- and First-Order Kinetic Model of the Degradation of TCE and *cis*-DCE with Commercial Iron'. *Environmental Science and Technology*, 1999, **33** (23) pp. 4304-4309.

17. Johnson, T.L., Scherer, M.M., and Tratnyek, P.G., 'Kinetics of Halogenated Organic Compound Degradation by Iron Metal'. *Environmental Science and Technology*, 1996, **30** (8) pp. 2634-2640.

18. Scherer, M.M., Balko, B.A., Gallagher, D.A., and Tratnyek, P.G., 'Correlation Analysis of Rate Constants for Dechlorination by Zero-Valent Iron.' *Environmental Science and Technology*, 1998, **32** (19) pp. 3026-3033.

19. Agrawal, A., Ferguson, W.J., Gardner, B.O., Christ, J.A., Bandstra, J.Z., and Tratnyek, P.G., 'Effects of Carbonate Species on the Kinetics of Dechlorination of 1,1,1-Trichloroethane by Zero-Valent Iron'. *Environmental Science and Technology*, 2002, **36** (20) pp. 4326-4333.

20. Boronina, T., Klabunde, K.J., and Sergeev, G., 'Destruction of Organohalides in Water Using Metal Particles: Carbon Tetrachloride/Water Reactions with Magnesium, Tin and Zinc'. *Environmental Science and Technology*, 1995, **29** (6) pp. 1511-1517.

21. Boronina, T.N., Lagadic, I., Sergeev, G.B., and Klabunde, K.J., 'Activated and Nonactivated Forms of Zinc Powder: Reactivity Toward Chlorocarbons in Water and AFM Studies of Surface Morphologies'. *Environmental Science and Technology*, 1998, **32** (17 Sep 1) pp. 2614-2622.

22. Cheng, S.F. and Wu, S.C., 'The Enhancement Methods for the Degradation of TCE by Zero-Valent Metals.' *Chemosphere*, 2000, **41** (8) pp. 1263-1270.

23. Wang, C.-B. and Zhang, W.-X., 'Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs'. *Environmental Science and Technology*, 1997, **31** (7) pp. 2154-2156.

24. Zhang, W.-X., Wang, C.-B., and Lien, H.-L., 'Treatment of Chlorinated Organic Contaminants with Nanoscale Bimetallic Particles'. *Catalysis Today*, 1998, **40** pp. 387-395.

25. Schrick, B., Blough, J.L., Jones, A.D., and Mallouk, T.E., 'Hydrodechlorination of Trichloroethylene to Hydrocarbons Using Bimetallic Nickel-Iron Nanoparticles'. *Chem. Mater.*, 2002, **14** pp. 5140-5147.

26. Lien, H.-L. and Zhang, W.-X., 'Nanoscale Iron Particles for Complete Reduction of Chlorinated Ethenes'. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2001.

27. Muftikian, R., Nebesny, K., Fernando, Q., and Korte, N., 'X-ray Photoelectron Spectra of the Palladium-Iron Bimetallic Surface Used for the Rapid Dechlorination of Chlorinated Organic Environmental Contaminants'. *Environmental Science and Technology*, 1996, **30** (12) pp. 3593-3596.

28. Kim, Y.-H. and Carraway, E.R., 'Dechlorination of Pentachlorophenol by Zero Valent Iron and Modified Zero Valent Irons'. *Environmental Science and Technology*, 2000, **34** (10) pp. 2014-2017.

29. Alessi, D.S. and Li, Z., 'Synergistic Effect of Cationic Surfactants on Perchloroethylene Degradation by Zero-Valent Iron'. *Environmental Science and Technology*, 2001, **35** (18) pp. 3713-3717.

30. Loraine, G.A., 'Effects of Alcohols, Anionic and Nonionic Surfactants on the Reduction of PCE and TCE by Zero-Valent Iron'. *Water Research*, 2001, **35** (6) pp. 1453-1460.

31. Bizzigotti, G.O., Reynolds, D.A., and Kueper, B.H., 'Enhanced Solubilization and Destruction of Tetrachloroethylene by Hydroxypropyl-β-cyclodextrin and Iron'. *Environmental Science and Technology*, 1997, **31** (2) pp. 472-478.

32. Hung, H.-M. and Hoffmann, M.R., 'Kinetics and Mechanism of the Enhanced Reductive Degradation of CCl4 by Elemental Iron in the Presence of Ultrasound'. *Environmental Science and Technology*, 1998, **32** (19) pp. 3011-3016.

33. Joo, S.H., Feitz, A.J., and Waite, T.D., 'Oxidative degradation of the Carbothioate Herbicide, Molinate, Using Nanoscale Zero-Valent Iron', *Environmental Science and Technology*, 2004, **38** pp. 2242-2247.

34. Ghauch, A., Rima, J., Amine, C., and Martin-Bouyer, M., 'Rapid Treatment of Water Contaminated with Atrazine and Parathion with Zero-valent Iron'. *Chemosphere*, 1999, **39** pp. 1309-1315.

35. Ghauch, A., Gallet, C., Charef, A., Rima, J., Martin-Bouyer, M.,,, 'Reductive Degradation of Carbaryl in Water by Zero-Valent Iron'. *Chemosphere*, 2001, **42** (4) pp. 419-424.

36. Walling, C., 'Fenton's Reagent Revisited'. *Accounts of Chemical Research*, 1975, **8** (125) pp. 1975.

37. Bossmann, S.H., Oliveros, E., Gob, S., Siegwart, S., Dahlen, E.P., Payawan, L.J., Straub, M., Worner, M., and Braun, A.M., 'New Evidence against Hydroxyl Radicals as Reactive Intermediates in the Thermal and Photochemically Enhanced Fenton Reactions'. *Journal of Physical Chemistry A*, 1998, **102** (28) pp. 5542-5550.

38. Kremer, M.L., 'Mechanism of the Fenton reaction. Evidence for a new intermediate'. *Physical Chemistry Chemical Physics*, 1999, **1** (15) pp. 3595-3605.

39. Leslie, D.R. and Ward, J.R., *Metal-ion Catalyzed Oxidation of a G-agent Simulant by Oxone*, Report no: CRDEC-TR-374. 1992, Melbourne. Chemical Research, Development & Engineering Center.

40. Giletto, A., White, W., Cisar, A.J., Hitchens, G.D., and Fyffe, J., *Reactive Decontamination Formulation*, US Patent No: 6,569,353. Issued: May 27 2003, Available at: <http://www.lynntech.com/licensing/patents/6569353.shtml>.

41. Aguila, A., O'Shea, K.E., Tobien, T., and Asmus, K.-D., 'Reactions of Hydroxyl Radical with Dimethyl Methylphosphonate and Diethyl Methylphosphonate. A Fundamental Mechanistic Study'. *Journal of Physical Chemistry A*, 2001, **105** (33) pp. 7834-7839.

42. Hynes, A.J., Stoker, R.B., Pounds, A.J., McKay, T., Bradshaw, J.D., Nicovich, J.M., and Wine, P.H., 'A Mechanistic Study of the Reaction of OH with Dimethyl-d_6

Sulfide. Direct Observation of Adduct Formation and the Kinetics of the Adduct Reaction with O_2.' *Journal of Physical Chemistry*, 1995, **99** (46) pp. 16967-16975.

43. Barnes, I., Becker, K.H., and Patroescu, I., 'FTIR Product Study of the OH Initiated Oxidation of Dimethyl Sulphide: Observation of Carbonyl Sulphide and Dimethyl Sulphoxide'. *Atmospheric Environment*, 1996, **30** (10-11) pp. 1805-1814.

44. Turnipseed, A.A., Barone, S.B., and Ravishankara, A.R., 'Reaction of OH with Dimethyl Sulfide. 2. Products and Mechanisms'. *Journal of Physical Chemistry*, 1996, **100** (35) pp. 14703-14713.

45. Domine, F., Ravishankara, A.R., and Howard, C.J., 'Kinetics and Mechanisms of the Reactions of CH_3S, CH_3SO, CH_3SS with O_3 at 300K and Low Pressures'. *Journal of Physical Chemistry*, 1992, **96** (5) pp. 2171-2178.

46. Barone, S.B., Turnipseed, A.A., and Ravishankara, A.R., 'Reaction of OH with Dimethyl Sulfide (DMS). 1. Equilibrium Constant for OH + DMS Reaction and the Kinetics of the OH–DMS + O_2 Reaction'. *Journal of Physical Chemistry*, 1996, **100** (35) pp. 14694-14702.

47. Urbanski, S.P., Stickel, R.E., and Wine, P.H., 'Mechanistic and Kinetic Study of the Gas-Phase Reaction of Hydroxyl Radical with Dimethyl Sulfoxide'. *Journal of Physical Chemistry A*, 1998, **102** (51) pp. 10522-10529.

48. Watts, S.F., Brimblecombe, P., and Watson, A.J., 'Methanesulphonic Acid, Dimethyl Sulphoxide and Dimethyl Sulphone in Aerosols'. *Atmospheric Environment*, 1990, **24A** (2) pp. 353-359.

49. Atkinson, R., 'Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds under Atmospheric Conditions'. *Chemical Reviews*, 1985, **85** (1) pp. 69-201.

50. Weres, O. and Pocekay, J., *Decontamination System Utilizing Hydrogen Peroxide, UV Light and Catalytic Surfaces*, Report no: CRDEC-CR-111. 1992, Vineburg. Chemical Research, Development & Engineering Center.

51. Doong, R.-A. and Chang, W.-H., 'Photoassisted Iron Compound Catalytic Degradation of Organophosphorous Pesticides with Hydrogen Peroxide'. *Chemosphere*, 1998, **37** (13) pp. 2563-2572.

52. Yang, Y.-C., Baker, J.A., and Ward, J.R., 'Decontamination of Chemical Warfare Agents'. *Chemical Reviews*, 1992, **92** (8) pp. 1729-1743.

53. Fleming, B.C. and McGrath, C.J., 'Integrated Zero-Valent Iron and Dark Oxidation Processes for In-situ Remediation of Explosives in Groundwater', [Internet] USACE Environmental Development Workshop 2001,

<http://hq.environmental.usace.army.mil/edw2001/abstracts/ZVIAbstractUSACE.pdf> last updated: 2001. [accessed 28/1/2004].

54. Oh, S.-Y., Chiu, P.C., Kim, B.J., and Cha, D.K., 'Enhancing Fenton Oxidation of TNT and RDX through Pretreatment with Zero-Valent Iron'. *Water Research*, 2003, **37** pp. 4275-4283.

55. Krishna, M.V.B., Chandrasekaran, K., Karunasagar, D., and Arunachalam, J., 'A Combined Treatment Approach using Fenton's Reagent and Zero-Valent Iron for the Removal of Arsenic from Drinking Water'. *Journal of Hazardous Materials*, 2001, **B84** (2) pp. 229-240.

56. Lindsey, M.E., Xu, G., Lu, J., and Tarr, M.A., 'Enhanced Fenton Degradation of Hydrophobic Organics by Simultaneous Iron and Pollutant Complexation with Cyclodextrins'. *The Science of the Total Environment*, 2003, **307** pp. 215-229.

57. Schmid, G., 'Metals', IN: *Nanoscale Materials in Chemistry* (Ed, K.J. Klabunde) 2001, John Wiley & Sons, New York, pp. 15-59.

58. Ponder, S.M., Ford, J.R., Darab, J.G., and Mallouk, T.E., 'Ferragels: A New Family of Materials for Remediation of Aqueous Metal Ion Solutions'. *Scientific Basis for Nuclear Waste Management XXII. Symposium (Materials Research Society Symposium Proceedings Vol.556). Mater. Res. Soc. 1999*, 1999 pp. 1269-76.

59. Smith, T.W. and Wychick, D., 'Colloidal Iron Dispersions Prepared via the Polymer-Catalyzed Decomposition of Iron Pentacarbonyl'. *Journal of Physical Chemistry*, 1980, **84** (12) pp. 1621-1629.

60. Kickelbick, G., 'Concepts for the Incorporation of Inorganic Building Blocks into Organic Polymers on a Nanoscale'. *Progress in Polymer Science*, 2003, **28** (1 January) pp. 83-114.

61. Balogh, L. and Tomalia, D.A., 'Poly(Amidoamine) Dendrimer-Templated Nanocomposites. 1. Synthesis of Zerovalent Copper Nanoclusters.' *Journal of the American Chemical Society*, 1998, **120** (29) pp. 7355-7356.

62. Zhao, M. and Crooks, R.M., 'Intradendrimer Exchange of Metal Nanoparticles.' *Chemistry of Materials*, 1999, **11** (11) pp. 3379-3385.

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Nanoparticles – A Literature Review

Lyndal McDowall

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19. ABSTRACT
The ultimate aim of researchers in the area of decontamination is to develop the perfect decontaminant - a substance that will degrade all contaminants but will leave surfaces and environments unharmed. Published research into zero-valent metal particles (ZVMs), in particular iron, shows that these particles, particularly those whose size is on the nanoscale, have the potential to be used as a decontaminant. This report examines the literature on nanoscale ZVMs, their potential use as decontaminants and ways to enhance their activity. Most of the research to date has looked at the reductive potential of ZVMs but it has been reported that zero-valent iron (ZVI) can actually catalyse oxidative degradation in a Fenton-type reaction. Thus this report also explores Fenton-type degradation of chemical warfare agents. The report also examines methods of incorporating nanoscale ZVM particles onto solid supports which may be useful for increasing the lifetime, activity and usability of the particles. Finally, possible challenges to developing ZVMs as a decontaminant are discussed.